

PATENT SPECIFICATION

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(21) Application No. 15489/76 (22) Filed 15 April 1976
 (31) Convention Application No. 568542
 (32) Filed 16 April 1975 in
 (33) United States of America (US)
 (44) Complete Specification published 13 Dec. 1978
 (51) INT CL² B01J 2/20
 (52) Index at acceptance
 CIA N4A1A N4B



(54) SPHEROIDAL ALUMINA PARTICLES

(71) We, UOP INC., a corporation organized under the laws of the State of Delaware, United States of America, of No. Ten UOP Plaza, Algonquin & Mt. Prospect Roads, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of spheroidal alumina particles. Spheroidal alumina particles offer numerous advantages, particularly when employed as a catalyst, or as a catalyst base or support, in a fixed bed type of operation. When so employed, said particles permit more uniform packing of the bed whereby variations in pressure drop across the bed are minimised, and the tendency of a reactant stream to channel through the bed out of effective contact with the catalyst is substantially obviated. Further, the spheroidal particles permit a more uniform and closely or tightly packed catalyst bed, and there are no sharp edges to break or wear off or disturb the compactness of the bed. This is of particular importance with respect to the catalytic conversion of hot exhaust gases from an internal combustion engine wherein the catalytic particles would otherwise tend to vibrate and eventually disintegrate under the constant buffeting of the hot, variable velocity exhaust gases.

It is an object of this invention to present a novel method for the manufacture of spheroidal alumina particles which, if possible, are thermally stable at conditions encountered in the treatment of hot exhaust gases from an internal combustion engine.

According to the present invention there is provided a method of manufacturing spheroidal alumina particles which comprises: (a) commingling a powdered alumina, an aluminium salt of a strong acid, a water-soluble surfactant and sufficient water to yield an extrudable mixture; (b) stirring or mulling the mixture until the decreasing viscosity of the mixture stabilises, and extruding the mixture; (c) segmenting and balling the

extrudate under the centrifugal influence of a spinning drum, with or without a prior preliminary segmenting step; and (d) drying and calcining the resulting spheroidal product.

Preferably, the powdered alumina utilized herein as a starting material is an alpha-alumina monohydrate of the boehmite structure such as is recovered as a by-product in the hydrolysis of aluminium alcoholates or alkoxides to produce alcohols. However, the alumina may be any of the various aluminium oxides or alumina gels such as boehmite, gibbsite or bayerite. Activated aluminas such as have been thermally treated with the elimination of at least a portion of the water and/or hydroxyl groups commonly associated therewith, may be employed. Of the activated aluminas, gamma- and eta-alumina, prepared by the thermal treatment respectively of boehmite and bayerite alumina at 400°—850°C., are particularly useful as a starting material.

The water-soluble surfactants used in the method of this invention, may be anionic, cationic or non-ionic surfactants. It is clearly desirable that they leave no residue harmful to the catalyst product in its intended use. Suitable surfactants include C₃—C₁₂ alcohols, linear primary alcohol polyethers, dimethyl-silicones, silicone polyether copolymers, and also the various and well-known polyoxyethylene alkylphenols, polyoxyethylene esters of fatty acids, polyoxyethylene alcohols, polyoxyethylene mercaptans, polyoxyethylene alkylamines, and polyoxyethylene alkylamides. A linear primary alcohol polyether, available under the trade name Antarox BL-240, is a particularly suitable surfactant. Preferably, the surfactant is utilised in an amount to comprise from 0.05 to 10 wt. % of the mixture to be extruded.

In accordance with the method of this invention, the mixture to be extruded further includes an aluminium salt of a strong acid. Suitable aluminium salts include aluminium chloride, aluminium sulphate and aluminium nitrate. Aluminium nitrate is preferred. The aforesaid alumina and aluminium salt are

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suitably employed in a weight ratio of from 5:1 to 20:1.

Pursuant to the method of this invention, sufficient water is added to form an extrudable mixture. Preferably, an amount of water is added to form an extrudable mixture having a weight loss on ignition at 900°C. of less than 60 wt. %, more preferably of from 15 to 45 wt. %. The mixture herein contemplated is thixotropic in nature, and it is desirable to stir or mull the mixture for only a brief period as the viscosity of the mixture decreases, typically a period of from 5 to 35 minutes depending on the volume of the mixture, with little if any stirring or mulling after the viscosity of the mixture is stabilised or reaches a steady state. The extrusion operation is suitably effected with commercial extrusion apparatus. For example, the mixture may be continuously processed through a cylinder by means of a rotating screw, and pressured through a die plate comprising a multitude of uniform openings designed to produce extrudate lengths of desirable shape and size, for example, from 1/32 to 1/2 in. (0.08 to 1.27 cm) in diameter.

The resulting extrudate, recovered from the extruder in the form of strands of indefinite length, is a moist but frangible, semi-plastic material readily segmented or broken into random lengths. Pursuant to the present invention, the extrudate is segmented and balled under the centrifugal influence of a spinning drum (e.g. a bowl), a process known to the art as marumerising. (Marumerizer is a Registered Trade Mark.) While the strands of extrudate may be segmented or broken into random or definite lengths prior to treatment in the spinning drum, it is a preferred practice to amass the strands and break the same into segments under the centrifugal force generated by the spinning drum, and the segments ultimately rolled and compacted into spheroidal particles of substantially uniform size and shape. As the particles are rolled en masse in the spinning drum, they invariably acquire a smooth but irregular or dimpled peripheral surface and consequently a greater peripheral surface area than would otherwise be the case. This is of particular significance with respect to the catalytic conversion of exhaust gases from an internal combustion engine.

The spheroidal product is subsequently dried, for example at a temperature of from 100° to 150°C. in air, and then calcined or oxidized, for example at a temperature of from 525° to 1100°C. The calcining process is suitably effected at a temperature of from 525° to 775°C. in air containing from 1 to 5 wt. % steam, and over a period of from 1 to 4 hours. It is a preferred practice to calcine the spheroidal product in air containing from 1 to 5 wt. % steam at a temperature of from 525° to 775°C., and to there-

after further calcine the product in air for a period of from 1 to 4 hours at a temperature of from 875° to 1100°C.

The last-mentioned calcining treatment serves a dual purpose. First, it serves to pre-shrink the spheroidal particles and thus preclude a subsequent and damaging shrinkage when disposed in a tightly packed catalyst bed and exposed to extreme temperatures such as are encountered, for example, in the treatment of hot exhaust gases from an internal combustion engine. And the calcining treatment has a further significant advantage. Said treatment has been found to impart desirable macropore characteristics to the spheroidal particles, provided that the spheroidal particles have been otherwise prepared as herein directed. For example, at given calcination temperature, when either the surfactant or the aluminium salt are omitted from the extrusion mixture, the desirable macropore characteristics are observed to a much lesser degree. The macropore characteristics of the preshrunk spheroidal particles of this invention include a total macropore volume in the range of from 0.6 to 0.16 cc per gram with substantially all of said volume being associated with pores in the 117-3500 Angstrom range as measured by a mercury porosimeter, and at least 25% of said volume being associated with pores in the 300-3500 Angstrom range.

In the conversion of exhaust gases from an internal combustion engine, other catalytic components are advantageously employed in conjunction with the spherical alumina particles of this invention to realise a catalyst composition of improved strength at high temperature. Other catalytic components include the metals and the oxides of metals of Groups IB, VIB, and VIII of the Periodic Table. Said catalytic components thus include the chromium, molybdenum, tungsten, iron, nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium, osmium, copper, and the like, in either the oxidised or the reduced form. It is understood that although improved catalyst strength is realised at high temperature, the activity, stability and auto-initiating temperature, lead susceptibility and other characteristics of the various catalytic components are not necessarily equivalent.

In the conversion of exhaust gases from an internal combustion engine, the catalyst composition is conveniently placed in a suitable container or catalytic converter which may be of the through-flow, cross-flow or radial-flow design and may supplant or be combined with the conventional acoustic muffler. The injection of supplemental air ahead of the converter inlet, generally by means of an aspirator or an external compressor, may or may not be required depending on the engine operating conditions and/or the particular catalytic components employed.

The following examples are present in illustration of the method of this invention and are not intended as a limitation on the generally broad scope of the invention as set out in the appended claims.

the spheres were dried at 125°C. and calcined in a flow of air containing about 3 wt. % steam for 2 hours at 650°C. There was no further calcination.

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EXAMPLE I

In the manufacture of spheroidal alumina particles according to the method of this invention, a 1950 milliliter aqueous solution of 180 grams of



and 30 grams of Anterox BL-240 (a linear primary alcohol polyether monionic surfactant) was milled with 3 kilograms of a finely powdered alpha-alumina monohydrate for about 30 minutes. The mixture was then extruded at about 150 psi (11 atm.) to form an extrudate about 1/8 in. (0.3 cm.) in diameter. The extrudate was loaded into the drum of a commercial marumeriser and the drum was spun about its vertical axis for about 50 seconds at 1100 rpm, 60 seconds at 550 rpm, and 60 seconds at 300 rpm. The marumerised spheres were recovered, dried at 125°C. and calcined. Calcination was in a flow of air containing about 3 wt. % steam for about 2 hours at 650°C., and thereafter in dry air at 1023°C. for 2 hours.

In this example, the spheres were again prepared as in Example I except that nitric acid was substituted for aluminium nitrate in the extrusion mix, and the surfactant was omitted. Thus, in the preparation of the extrusion mix, a 1950 milliliter aqueous solution of 190 grams of 4 wt. % nitric acid was milled with 3 kilograms of a finely powdered alpha-alumina monohydrate for about 30 minutes. The mixture was then further treated in the described manner.

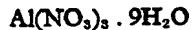
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EXAMPLE III

Alumina spheres were again prepared as described in Example I, except that in this case the surfactant was omitted from the extrusion mix. Thus, a 1950 milliliter aqueous solution of 180 grams of

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was milled with 3 kilograms of a finely powdered alpha - alumina monohydrate for about 30 minutes. The mixture was then further treated in the described manner.

The physical properties of the spheroidal alumina product of each of the above examples is set out in Table I below.

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EXAMPLE II

Alumina spheres of this example were prepared as described in Example I except that

TABLE I

Example	I	II	III	IV
Surface Area, m ² /gm	50		133	
Crushing Strength, kg	10.3	12.4	6.12	10.0
Av. Bulk Density, gms/cc	0.751	0.643	0.758	0.778
Macropore Volume, cc/gm	0.4838	0.0175	0.4916	0.4169
1750—58,333 Å	0.0063	0.0065	0.0079	0.0042
300—1750 Å	0.2240	0.0034	0.0477	0.0071
117—300 Å	0.2535	0.0076	0.04360	0.4056

WHAT WE CLAIM IS:—

1. A method for manufacturing spheroidal alumina particles which comprises:
 - (a) commingling a powdered alumina, an aluminium salt of a strong acid, a water-soluble surfactant, and sufficient water to yield an extrudable mixture;
 - (b) stirring or mulling the mixture until the decreasing viscosity of the mixture stabilises, and extruding the mixture;
 - (c) segmenting and balling the extrudate under the centrifugal influence of a spinning drum, with or without a prior, preliminary segmenting step; and
 - (d) drying and calcining the resulting spheroidal product.
2. The method of Claim 1 wherein the alumina in step (a) is alpha-alumina monohydrate.
3. The method of Claim 1 or 2 wherein the aluminium salt in step (a) is aluminium nitrate.
4. The method of any of Claims 1 to 3 wherein the surfactant in step (a) is a linear primary alcohol polyether.
5. The method of any of Claims 1 to 4 wherein the alumina in step (a) is employed in from a 5:1 to a 20:1 weight ratio with the aluminium salt.
6. The method of any of Claims 1 to 5 wherein the surfactant in step (a) comprises from 0.05 to 10 wt. % of the mixture.
7. The method of any of Claims 1 to 6 wherein the mixture in step (a) has a weight

alumina in step (a) is alpha-alumina monohydrate.

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loss on ignition at 900°C. of less than 60 wt. %.

8. The method of any of claims 1 to 7, wherein the stirring or mulling in step (b) is effected for from 5 to 35 minutes.

9. The method of any of claims 1 to 8 wherein the calcining in step (d) is effected at a temperature of from 525° to 1100°C.

10. The method of any of claims 1 to 8 wherein the calcining in step (d) is effected over a period of from 1 to 4 hours at a temperature of from 525° to 775°C in air containing from 1 to 5 wt. % steam, and thereafter for a period of from 1 to 4 hours at a temperature of from 875° to 1100°C in air.

11. A method for manufacturing spheroidal alumina particles carried out substantially as described in either of the foregoing Examples I and II.

12. Spheroidal alumina particles whenever manufactured in accordance with the method of any of claims 1 to 11.

13. A catalyst for the conversion of internal combustion engine exhaust gases comprising spheroidal alumina particles made by the method of any of claims 1 to 11 in association with a metal or oxide of Group IB, VIB or VIII of the Periodic Table.

14. A process for the conversion of internal combustion engine exhaust gas wherein the gas is contacted with a catalyst as claimed in claim 13.

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Chartered Patent Agents,
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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1978
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.